

A Survey: The Chemical Compatibility of Silicon Carbide with Molten Fluoride Salts

Jo Jo Lee, Yutai Katoh, Takaaki Koyanagi, Lauren Garrison, Wilna Geringer

Oak Ridge National Laboratory, One Bethel Valley Road, P.O. Box 2008, MS-6138, Oak Ridge, Tennessee 37831 USA, leeyj@ornl.gov

INTRODUCTION

Silicon carbide (SiC) and continuous fiber-reinforced SiC matrix composites (SiC_f/SiC) are promising high temperature materials with excellent mechanical strength, high thermal conductivity and low neutron absorption. High purity SiC and variants are candidate materials for structural and functional components of Fluoride Salt Cooled High Temperature Reactors (FHR). SiC_f/SiC composites are intended for construction of core support plates, internals and control rods while SiC from chemical vapor deposition (CVD) is an integral layer coating among carbon layers for TRISO fuel particles.

The chemical compatibility of SiC with molten fluoride salts is not well known. SiC will be exposed to diverse environments in FHR, such as oxidizing impurities, metals and graphite in the salt melt. Corrosion of SiC in fluoride molten salts involves galvanic reactions combined with acid-base reactions at the SiC/melt interface.

The main objectives of this survey are: 1) to summarize the key research concepts and 2) to identify technical gaps for understanding the chemical compatibility of SiC with fluoride molten salt, namely eutectic FLiBe (67LiF-33BeF₂) and FLiNaK (46.5LiF-11.5NaF-42KF).

Literature survey

Very little is known about the corrosion potential and solubility of SiC in molten fluoride salts. SiC and variants have only recently been tested in FLiBe and FLiNaK molten salts in limited conditions [1-3]. The salt melt is a diverse chemical environment and the two main corrosion situations are: 1) galvanic corrosion of SiC initiated by the presence of container alloys/structural materials; and 2) the effect of oxidants (O₂, moisture, metal oxides), fluoride compounds, and other impurities (H₂ and transmutants) on corrosion of SiC.

The chemical stability of SiC should be tested in diverse chemical environments. When two dissimilar metals are in contact with each other, an uneven balance of electrons drives cathodic reactions, such as those that decompose SiC. Galvanic couples occur when there is a potential difference that occurs between two dissimilar metals. Prediction of corrosion behavior and development of potential protective coatings will depend on identifying galvanic couples and control of corrosion potentials.

1. Hastelloy N and its corrosion products

Hastelloy N is a Ni-based superalloy used for container and salt-containing piping for FHR. In a study of CVD SiC corrosion, when Hastelloy N was exposed to FLiNaK at 700 °C with NiF₂ (Ni²⁺) for 15 days and 45 days, molten salt forming fluorides, such as NiF₂, initiated SiC corrosion which proceeded through Ni₃Si₁₂ silicide formation [1]. Ni, Cr, Fe and Mo tend to diffuse outward to the alloy surface. Fe and Mo accumulate near the surface but Cr and Ni dissolve into the salt melt. Cr is the most reactive alloy constituent and dissolves in the melt to form fluoride compounds like CrF₂ (Cr²⁺) and CrF₃ (Cr³⁺). Preliminary results show that Cr³⁺ drives Si out of SiC resulting in C- and O-rich phases, and Cr forms carbides (Cr₇C₃, Cr₃C₂) [4]. Silica (SiO₂) is often associated with CVD SiC. Studies have shown that it can dissolve in molten fluoride salts, adding O to the melt, depending on the electrochemical potential [5].

2. The role of oxygen

The stability of fluorides has been somewhat investigated with Hastelloy N and metal fluoride corrosion products but not to the same extent with oxides. The instability of SiC in air is well known, as silica scales and passivation have been studied extensively for non-nuclear applications in refractories and power electronic industries. Oxygen, moisture and hydrogen tend to be common trace impurities in the molten salt environment during normal operating conditions.

For FHR, the stability of oxides and fluorides in relation to each other are not well known. Highly crystalline composites of SiC are desired because of a stronger chemical bond with Si and C. Single crystal SiC and very high purity CVD SiC (.999995%) were only slightly corroded in FLiNaK at 700 °C for 10 and 45 day periods in one study [6]. Oxygen contamination of FLiNaK was the likely source for initiating slight corrosion of SiC. In another study, the interlayer boundary of SiC matrix in SiC_f/SiC has been shown to be preferentially oxidized. SiC matrix has higher intrinsic oxygen content due to repetitive densification during fabrication [3]. A non-uniform corrosion was observed when SiC was tested in FLiNaK at 800, 900 and 1000 °C for 500-hour periods with an increase in severity of corrosion and matrix exfoliation as corrosion test temperature was increased. Non-uniformity of SiC can cause temperature gradients in the material resulting in mass transfer.

3. H_2 and transmutant interactions

Transmutant corrosion of container alloys in molten fluoride salt could also initiate the corrosion of SiC. FLiBe can produce tritium in the form of TF under neutron irradiation but mainly H as T along with O, F, He etc. through transmutation. In an in-situ tritium release experiment for the force-free helical reactor (FFHR) FLiBe blanket system, tritium release (H_2 activity and F^- activity) and corrosion behavior depended on the redox potential in the system. TF evolves to HT to T_2 with increasing P_{H_2} . T_2 has the lowest solubility among the released tritium forms in FLiBe and tends to permeate through structural walls more readily than other released tritium species. The T generated by T_2 has a large diffusivity in structural materials. Redox control is key to select and develop tritium recovery systems and confinement systems in the FLiBe blanket system for FFHR [7].

TECHNICAL GAP ANALYSIS

The literature survey encompasses the key research concepts and anticipated technical issues with SiC stability in a molten fluoride salt environment. There have been some significant R&D efforts to characterize SiC and study its corrosion behavior since the 1950's but mostly for high temperature non-nuclear applications and in static systems.

The corrosion of SiC for FHR will likely be a galvanic reaction coupled with chemical and diffusive processes at the SiC/melt interface. Currently, there are only preliminary studies on individual reactions at high temperature. Well-controlled and repeatable experiments are needed to fully evaluate the effect of oxides, fluorides, salt impurities and transmutants on SiC corrosion. The following technology gaps are highlighted:

- *There is a significant lack of experimental validation of SiC compatibility with materials optimized for use in fluoride molten salt for FHR.*
- *The corrosion kinetics of SiC during normal operating conditions and accident conditions are not well understood.*
- *Redox/corrosion potential measurements and solubility limits are needed so that phase stability, corrosion products and corrosion behavior may be predicted and controlled.*
- *A full electrochemical view of SiC corrosion is lacking. Stability diagrams for SiC in FLiBe and FLiNaK are two important research milestones.*
- *The knowledge gained from other reactors systems and tritium interactions are an important basis to start similar investigations with SiC for FHR.*

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